ECCE12
The 12th EUROPEAN CONGRESS OF CHEMICAL ENGINEERING
Florence 15-19 September 2019

Development of a catalyst for oxidative coupling of methane in a gas-solid vortex reactor

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Highlights

- Synthesis of a thermally and mechanically stable catalyst for OCM in a GSVR.
- First demonstration of oxidative coupling of methane in GSVR.
- Process intensification of OCM

1. Introduction

Oxidative coupling of methane (OCM) is a promising pathway for the direct synthesis of C_2 hydrocarbons from methane according to the following global chemical reactions.[1]

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \qquad \Delta H_r^0 = -282 \text{ kJ mol}^{-1} \qquad (1)$$

$$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O \qquad \Delta H_r^0 = -177 \text{ kJ mol}^{-1} \qquad (2)$$

The presence of oxygen and the high reaction temperature can facilitate the overoxidation of reactants and products to CO and CO_2, typically limiting the C_2 hydrocarbon yields to below 30%.[2]

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_r^0 = -801 \text{ kJ mol}^{-1} \qquad (3)$$

The high reaction exothermicity moreover dictates the need for a suitable heat management strategy.

In a gas-solid vortex reactor (GSVR), a rotating fluidized bed of solids is obtained by the tangential injection of gas at high velocities (Figure 1).[3] In the bed, the centrifugal forces on the catalyst particles balance the drag forces, leading to a dense and uniform bed. The very high gas-solid slip velocities intensify interfacial transfer of mass, energy and momentum, allowing a reduction in gas phase residence time. Using extensive computational fluid dynamics (CFD) simulations, a gas-solid vortex reactor has been designed and commissioned at Ghent University[3]**Error! Reference source not found.**. The diameter of the reaction chamber is 80 mm, containing 8 inlet slots with a width of 1 mm (Figure 1).[3]**Error! Reference source not found.**

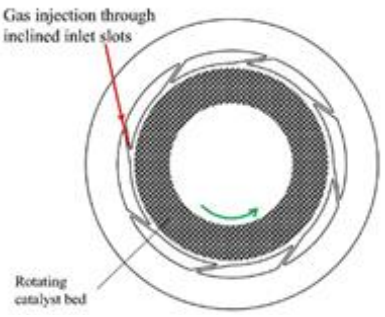

Figure 1 . Top view and operation of a gas solid vortex reactor in static geometry

Using bifurcation analysis incorporating detailed microkinetic models, Vandewalle et al. [4] showed that the good thermal back mixing combined with limited species back mixing in the GSVR can potentially improve C_2 yields when the reactor is operated on an ignited branch close to the extinction state. [5]

The high reaction temperature, the high solid velocities, and the low space times in the GSVR at those conditions require the development of a novel catalyst with high attrition resistance, high

thermal stability, high activity, and proper size distribution. In this presentation, we report the development of such a supported catalyst, and compare its performance in a fixed bed reactor with that in the GSVR.

2. Results and Discussion

Cold flow experiments were performed in the GSVR with inlet gas flow rates in the range of 15-30 $Nm^3\ hr^{-1}$, and slot velocities exceeding 100 m s^{-1} to test the stability of the catalyst bed and its attrition resistance. Under these conditions, a stable bed of 10 g of catalyst material with a thickness of about 10 mm could be retained in the GSVR at room temperature for a duration of 1 hour (Figure 2a). Over the 1 hour experiment, less than 1% of the material was entrained. Similar experiments with conventional Sr/La_2O_3 OCM catalyst pellets and with inert α-Al_2O_3 pellets resulted in rapid attrition and entrainment of the pulverised pellets with the gas stream. The gas flow rates and the catalyst material holdup in the GSVR correspond to very low space times of 0.1 $kg_{cat}\ s\ mol^{-1}{}_{CH4,0}$. For these space times, the synthesized catalyst material was tested in a quasi-isothermal fixed bed reactor at 800 °C and for a O_2:CH_4 inlet ratio of 4. A reasonable C_2 selectivity of 40-50% and a CH_4 conversion of 5-10 % were obtained for this high activity catalyst (Figure 2b). Typical OCM catalysts like Li/MgO and $NaMnWO_4/SiO_2$ show essentially no CH_4 conversion for space times below 5.0 $kg_{cat}\ s\ mol^{-1}{}_{CH4,0}$. [6] Next, the synthesized catalyst will be tested under reactive conditions in the GSVR. Based on detailed microkinetic simulations based on the fixed-bed experiments a methane conversion of 4% and a C_2 selectivity of 45% are expected.

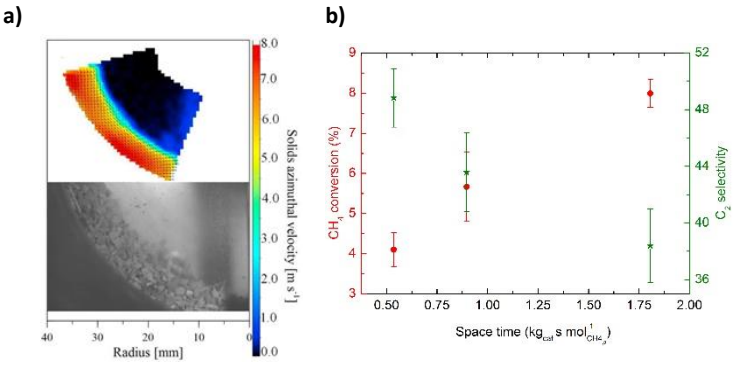

Figure 2 a) Azimuthal velocity of solids in the GSVR [3] and b) CH_4 conversion and C_2 selectivity vs. space time for synthesized catalyst at 800 °C

3. Conclusions

A thermally and mechanically stable OCM catalyst material was synthesized, which forms a stable catalyst bed under the harsh conditions in the GSVR reactor. At the conditions and at low space times, the synthesized catalyst material displayed a methane conversion between 5 and 10 % and a C_2 selectivity around 50%. Detailed simulations indicate that a similar performance can be expected in the GSVR. These proof-of-concept experiments are currently scheduled and will be reported at the conference.

References

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